SYNTHESIS AND METHODS DEVELOPMENT OF ADSORBENTS BASED ON POLY (STYRENE-DIVINYLBENZENE) DERIVATIVES FOR SOLID PHASE EXTRACTION OF AROMATIC COMPOUNDS

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To my beloved is my Father (Drs. Abdullah Siregar), to my beloved my mother (Dra. Mardiah Matondang), to my twin sister (Sri Helmi Siregar, ST), and my brother in law (Teguh Wahyudi), my sisters (Maria Ulfah Siregar, S.Kom. , Nila Franila Siregar, S.H., Isma Fahdiani Siregar, A.md.), and to my younger brother
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There's nothing in life that makes me happier than loving all of you
Giving help and comfort to each other

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ABSTRACT

In this study, poly (styrene-divinylbenzene) (PS-DVB) adsorbents were synthesized by using suspension polymerization method. The modifications on highly cross-linked porous PS-DVB resin consisted of (i) Friedel-Crafts acylation reaction using stearoyl chloride as an acylation agent to produce PS-DVB heptadecyl ketone, (ii) Chloromethylation reaction to produce chloromethyl PS-DVB in the presence of chloromethyl styrene, and (iii) Williamson ether reaction using sodium metal and octadecanol as reaction agents to produce octadecoxy methyl PS-DVB. The synthesized adsorbents were characterized by Fourier transform infrared (FTIR), scanning electron microscopy (SEM), nitrogen adsorption analysis and thermogravimetric analysis (TGA). Solid phase extraction (SPE) studies of selected organic test compounds, namely nitrobenzene, 2-chlorophenol, benzaldehyde, butyrophenone, and *p*-cresol were carried out using SPE tubes packed with the synthesized adsorbents. Commercial SPE adsorbents were also used for comparison. The recoveries obtained for the home-made PS-DVB were in the range of 7% to 72% with relative standard deviations of 1% to 10%. Increased percentages of recovery (35%-83%) with the relative standard deviations of 2%-7% were obtained using PS-DVB heptadecyl ketone. Highest recovery percentages (67%-100%) were obtained using commercial C_{18}-silica adsorbent. Breakthrough volume determinations for the various adsorbents showed that highest breakthrough volume was achieved for PS-DVB heptadecyl ketone adsorbent, i.e. 30.60 mL of 20 ppm nitrobenzene and 20.47 mL of 20 ppm 2-chlorophenol. Lowest breakthrough volume was obtained for octadecoxy methyl PS-DVB adsorbent (1.03 mL of 20 ppm nitrobenzene and 1.00 mL of 20 ppm 2-chlorophenol). PS-DVB heptadecyl ketone has been proven suitable to be used as SPE adsorbent in the future.

ABSTRAK

Dalam kajian ini, bahan penjerap poli(stirena-divinilbenzena) PS-DVB disintesis melalui kaedah pempolimeran ampaian. Pengubahsuaian dilakukan terhadap liang poros resin PS-DVB melalui kaedah (i) Tindak balas pengasilan Friedel-Crafts menggunakan stearoil klorida sebagai agen pengasilan untuk menghasilkan PS-DVB heptadekil keton, (ii) Tindak balas pengklorometilan untuk menghasilkan klorometil PS-DVB dengan kehadiran klorometil stirena, dan (iii) Tindak balas eter Williamson menggunakan logam natrium dan oktadekanol sebagai agen tindak balas eter untuk menghasilkan oktadekoksi metil PS-DVB. Penjerap yang telah disintesis itu dilakukan pencirian menggunakan spektroskopi inframerah transformasi fourier (FTIR), molekul imbas elektron (SEM), analisis penjerap nitrogen and analisis termogravimetri (TGA). Kajian pengekstrakan fasa pepejal (SPE) bagi beberapa sebatian organik terpilih seperti nitrobenzena, 2-klorofenol, benzaldehid, butirofenon dan *p*-kresol dijalankan dengan menggunakan tiub SPE yang dipadatkan dengan penjerap yang disintesis. Bahan penjerap SPE komersial juga digunakan untuk perbandingan di dalam kajian ini. Perolehan semula yang dihasilkan untuk PS-DVB sintesis di dalam julat 7%-72% dengan nilai sisihan piawai relatif 1%-10%. Pertambahan peratus perolehan semula (35%-83%) dengan sisihan piawai relatif 2%-7% dihasilkan dengan menggunakan PS-DVB heptadekil keton. Peratus perolehan semula yang tertinggi (67%-100%) dihasilkan oleh bahan penjerap C_{18}-silika komersial. Penentuan kemunculan isipadu untuk beberapa bahan penjerap menunjukkan bahawa kemunculan isipadu yang tertinggi dihasilkan oleh PS-DVB heptadekil keton, iaitu 30.60 mL untuk nitrobenzena 20 ppm dan 20.47 mL untuk 2-klorofenol 20 ppm. Kemunculan isipadu yang terendah dihasilkan oleh bahan penjerap oktadekoksi metil PS-DVB (1.03 mL untuk nitrobenzena 20 ppm dan 1.00 mL untuk 2-klorofenol 20 ppm. PS-DVB heptadekil keton terbukti sesuai digunakan sebagai bahan penjerap SPE di masa hadapan.

CONTENTS

LIST OF SYMBOL/ABBREVIATION/NOTATIONS/TERMS

PS-DVB	-	Poly(styrene-divinylbenzene)
SPE	-	Solid Phase Extraction
ppm	-	Parts per Million
GC	-	Gas Chromatogaphy
FID	-	Flame Ionization Detector
FTIR	-	Fourier Transform Infrared
IR	-	Infrared
p	-	Para
µL	-	Micro liter
mL	-	Mili Liter
v/v	-	Volume per Volume
KBr	-	Potassium Bromide
mg	-	Mili Gram
mm	-	Mili Meter
kPa	-	Kilo Pascal
M_X	-	Test Compound Concentration (ppm)
M_S	-	Internal Standard Concentration (ppm)
F_S	-	Internal Standard Response Factor
F_X	-	Test Compound Response Factor
A_S	-	Internal Standard Peak Area
A_X	-	Test Compound Peak Area
σ	-	Population Variance
n_1	-	Size of Sample
H_0	-	Null Hypothesis
H_1	-	Alternative Hypothesis
α	-	Level of Significance
v	-	Degree of Freedom

X	-	Mean
s	-	Standard Deviation
t_R	-	Retention Time
IS	-	Internal Standard
R.S.D.	-	Relative Standard Deviation
ODS	-	Octadecylsilica
%R	-	Percentage of Recovery
c	-	Effluent Concentation
c_0	-	Influent Concentration
$\boldsymbol{c/c_0}$	-	The ratio of Effluent Concentration to Influent Concentration.
SEM	-	Scanning Electron Microscopy
BET Method	-	Brunauer, Emmet and Teller Method
BJH Method	-	Barrer, Joiyner and Halenda Mehtod
TG	-	Thermogravimetric

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 General Background

Thousands of polymers have been synthesized and more are likely to be produced in the future. Functionalized polymers have found various applications as supports in solid phase synthesis, such as chromatographic packing, polymer supported catalysts and starting materials for the synthesis of ion exchange resins. The suspension copolymerization of styrene with divinylbenzene has been developed by Kun and Kunin [1] to produce poly(styrene-divinyl benzene) (PS-DVB). This material has been widely used as a stationary phase for high performance liquid chromatography (HPLC) and matrices of a great number of ion exchangers.

Previous workers [2] have found that macro-porous PS-DVB is prepared as a result of phase separation during the copolymerization in the presence of inert diluents. The inert diluents are extracted after copolymerization and porous structure is obtained. Polymers, solvents or non-solvents of polystyrene or mixture of them may be used as diluents giving various types of pore size distribution.

PS-DVB copolymers have a hydrophobic surface and overcome many of the limitations of bonded silicas, especially those related to the limited pH stability in the presence of the silanol group [3]. PS-DVB is often used as sorbents in reversed-phase (RP) liquid chromatography [4]. Usually, porous PS-DVB packing materials are employed because they provide a large surface area. Commercially available porous PS-DVB packing includes Amberlite XAD-2, PLRP-S, and PRP-1. While PS-DVB packing has many advantages, such as chemical stability at high and low pH and the absence of residual silanol groups, they suffer from the disadvantage of yielding lower chromatographic efficiencies than silica-based octadecylsilyl bonded phase packing of the same particle size.

Since 1990s, chemically modified resins have been developed and applied to the trace enrichment of polar substances. These sorbents have excellent hydrophobicity and yield higher recoveries than unmodified ones and have found great applications in solid phase extraction (SPE) for sample preparation in environmental analysis [5]. One of the possible chemical modifications of resin is by using Williamson ether reaction. The Williamson ether reaction was named after Alexander William Williamson (1824-1904). The Williamson ether synthesis is an example of a nucleophilic substitution reaction. The nucleophile is an alkoxide anion, which displaces a halide ion, typically chloride or bromide, from a primary haloalkane. The alkoxide can be generated by addition of metallic sodium to the corresponding alcohol. Although the Williamson ether synthesis is a general method for the laboratory production of ethers, there are some limitations to its use. Since the alkoxide ion is a strong base, their use is limited to primary unhindered alkylating agents. Otherwise, elimination competes strongly with the nucleophilic substitution for the reactant molecules. Sometimes, the reaction is run in a solvent, which fosters the SN_2 process [6-7].

Solid-phase extraction has recently come into the focus of interest and offers a viable alternative to the conventional sample preparation methods [5, 8, 9]. SPE has evolved to be a powerful tool for isolation and concentration of trace analytes in a variety of sample matrices. Nowadays, the most frequently used design in off-line SPE is the cartridge or the syringe barrel. They are usually made of polypropylene or polyethylene and filled with packing material having different functional groups.

The solid sorbent is contained between two 20-μm polypropylene frits. Cartridges vary from as little as 100 mg to 1 g or more. Syringe barrels range in size from 1 to 25 mL and packing weights from 50 mg to 10 g. Solvent reservoirs may be used at the top of the syringe barrels to increase the total volume (50-1000 mL) [8].

The breakthrough volumes can describe the characteristics of adsorbents. To record a breakthrough curve, after proper equilibration of the SPE cartridge, a solution of analyte is pumped directly to the detector (cartridge in the bypass position) to determine its absorbance signal. The cartridge is switched in-line causing the UV signal to drop to baseline level because the analyte is retained on the cartridge. Upon breakthrough, the UV signal will rise back to its initial level. The volume of analyte solution that can flow through the cartridge before breakthrough occurs is the "breakthrough volume" and is used as the measure of the extraction capacity [10].

This study was set to explore the methods of preparing of PS-DVB stationary phases, their modification, characterization, as well as application in analytical separation. PS-DVB beads were synthesized based on suspension polymerization from its monomers, styrene, and divinyl-benzene. A new PS-DVB modification method was carried out by introducing octadecoxy group ($C_{18}H_{37}$-0-) onto the PS-DVB back bone.

1.2 Problem Background

The beginning of the era of synthetic polymers for ion exchange is generally attributed to the work of B. A. Adams and E. L. Holmes at the Chemical Research Laboratory, Teddington, England [11]. Although the phenomenon of water softening by ion-exchange was known at the time of their collaboration, the deionization of water required stable materials capable of performing both cation and anion exchange.

A polymer is a chemical species of high molecular weight. It is made up of repeating low-molecular weight units. These repeating units are termed monomers and the compounds are reacted to form a polymer. There are two types of polymers namely, natural and synthetic polymers [12]. The PS-DVB polymers are manufactured as general sorbents and they are often chosen for SPE works because the loading properties of organic carbon are superior to those of silica-based adsorbent [13]. Leon-Gonzalez and co-workers [3] have found that the chemically modified PS-DVB resin can adsorbed wide variety of organic analytes efficiently. They have a higher sorption capacity for the more polar compounds than their unmodified analogues do.

Balakhrisnan and Ford [14] have found that the suspension polymerization is widely used in polymerization of styrene. The major factors controlling the particle size are surface tension, densities of aqueous and monomer phases, viscosities of aqueous and monomer phases, diameters of stirrer and kettle, and stirring speed. Their research on particle size effects in polymer supported organic synthesis and polymer supported phase transfer catalysis requires cross linked polystyrenes of a wide range of sizes with chloromethyl group that can be converted easily to polymer bound.

Masque *et al.* [5] described the application of unmodified and modified PS-DVB to the analysis of group of polar phenolic compounds. They have used on-line and the off-line SPE to determine pollutants in environmental waters. The advantages of on-line SPE are the higher sensitivity, absence of organic solvents and less manipulation of the samples, which leads to greater precision, and makes it easier for it to be automated. The functional polymer networks have gained great importance in many fields of scientific research as well as for industrial applications. The interest stems from the variety of possible modifications of their chemical and physical properties. Claudio *et al.* [15] said that increasing environmental concerns in waste water treatment has lead to the use of organic ligands anchored to solid supports in order to remove and recover important metal ions from aqueous solution.

The use of polymeric resins in reversed-phase high performance liquid chromatography (RP-HPLC) has grown dramatically, since an increasing number of polymeric columns are commercially available. The application of silica-based supports is limited by the low stability of silica at alkaline pH values and by the unwanted interactions between polar solutes and remaining free silanol groups not covered by the hydrophobic ligands. In particular, PS-DVB-based resins show a high stability over the pH range 1-14 and provide excellent separations. Additionally, PS-DVB particles permit the introduction of numerous functional groups that change their surface chemistry and hence the chromatographic selectivity [16].

Porous PS-DVB based resins have proven to be very effective for SPE of a wide variety of organic compounds from predominantly aqueous samples. Their effectiveness is enhanced by chemical introduction of polar groups, such as acetyl, and sulfonic acid [17]. However, these modified PS-DVB resins were poorly extracted small toward polar organic compounds such as alcohols, aldehydes, ketones and carboxilyc acids. Consequently, when SPE is carried out in extremely acidic or basic media, reversed-phase polymeric sorbents (generally based on PS-DVB) are used. The PS-DVB has much lower backgrounds due to improvements in manufacturing processes. The PS-DVB was used as an adsorbent material has demonstrated to provide improved recoveries for phenolic compounds as compared to the traditional and more commonly applied C_{18} material [17].

Silica based packing materials are widely used in high performance liquid chromatography (HPLC) because of their mechanical stability and wide variety of derivatizations, as well as their relatively higher column efficiency. Unfortunately, silica based supports also possess a series of drawbacks. One is their inherent low chemical stability at pH above 8 and below 2. This drawback can cause dissolution of the silica support and loss of the bonded phase. In general, ideal ion-exchange packing materials for HPLC are mechanically stable, chemically inert, hydrophilic with no irreversible adsorption, and highly efficient. To overcome the stability problem of silica, researchers have turned their attention to polymeric supports. PS-DVB-based supports have been studied and utilized the most, due to their chemical stability in both strong base and acid. Recently, HPLC ion exchange stationary phase have been developed from the PS-DVB matrix by applying a hydrophilic

coating on the surface. However, the column efficiency could not match that of most silica-based column [18]. It is of interest, therefore, to explore new techniques to treat the surface of PS-DVB beads in order to obtain more variable absorbent.

1.3 Aim and Objectives

1.3.1 Aim of Study

The aim of this study is to develop a new chemically modified PS-DVB resin by introducing octadecoxy group ($C_{18}H_{37}$-O-) onto the PS-DVB backbone. The new modified PS-DVB is compared with unmodified PS-DVB and other modified PS-DVB and these phases are applied as adsorbents in solid phase extraction.

1.3.2 Objectives of Study

The objectives of this study are:

a) To synthesize PS-DVB adsorbent using suspension polymerization technique.
b) To produce modified PS-DVB adsorbents by Friedel-Crafts acylation reaction, chloromethylation, and Williamson ether reaction.
c) To characterize and study the performance of the adsorbents.
d) To apply the developed modified PS-DVB resins to SPE analysis.

1.4 Scope of Study

The following are the scopes of study:

a. Preparation PS-DVB and modification of PS-DVB via
    i. Friedel-Crafts acylation
    ii. Chloromethylation
    iii. Williamson ether reaction

b. Study of the physical characteristics of PS-DVB and modified PS-DVB by using:
    i. Fourier transform infrared spectrophotometry (FTIR)
    ii. Scanning electron microscopy (SEM)
    iii. Thermogravimetric analysis (TGA)
    iv. Nitrogen adsorption analysis (NA)

c. Study of the chemical characteristics of PS-DVB and modified PS-DVB by using:
    i. Solid phase extraction (SPE)
    ii. Gas chromatography (GC)

1.5 Outline of the Thesis

This thesis consists of six chapters. Chapter 1 presents general background of this study, research aim, research objectives and scope. Chapter 2 compiles the literature reviews and theoretical background on PS-DVB, modification of PS-DVB and its application as an adsorbent for chemical analysis. The procedures for characterization and application of the synthesized materials are presented in Chapter 3. Chapter 4 reports the results and discusses the preparation of PS-DVB, and modified PS-DVB. Chapter 5 describes the characterization and application of unmodified and modified PS-DVB as an adsorbent in the chromatographic analysis. The concluding Chapter 6 summarizes this thesis by presenting the overall conclusions and suggestions for future study.

studies. Higher breakthrough volume for modified PS-DVB or PS-DVB polymeric resins are well expected by using the recommended elution solvents.

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